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Bio-accumulation of heavy metals in muscle tissues of a few benthic species in South Gujarat, India

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Original Article

Abstract

Three bottom feeder species, *Mugil curema*, *Boleopthalmus dussumieri,* and *Scylla serrata* collected from five different estuaries of South Gujarat, India were studied to determine the concentration of Cu, Zn, Pb, Cd, and Hg. Results indicated species-specific bio-accumulation which significantly varied between the stations. The heavy metal concentration in all the species varied in descending order of Cu>Zn>Pb>Hg>Cd. The concentration of Cu was predominant in *B. dussumieri* whereas *M. curema* and *S. serrata* recorded a higher concentration of Zn than other metals. The average concentration of Cu, Zn, Pb, Hg and Cd recorded in fishes were 6.77 mg kg^{-1}, 5.60 mg kg^{-1}, 0.37 mg kg^{-1}, 0.19 mg kg^{-1} and 0.01mg kg^{-1} wet weight respectively. Moreover the average concentration of Cu, Zn, Pb, Hg and Cd in crab was 4.67 mg kg^{-1}, 6.82 mg kg^{-1}, 0.36 mg kg^{-1}, 0.14 mg kg^{-1} and 0.0 mg kg^{-1} wet weight respectively. The bio-concentration factor (BCF) revealed the total metal concentration in biota was "low" in all the species with the maximum concentration in *M. curema* followed by *S. serrata* and *B. dussumieri.* The findings of the present study report a higher concentration of Pb (1.23 mg kg^{-1} wet weight in *M. curema*, 0.91mg kg^{-1} wet weight in *B. dussumieri* and 0.79 mg kg^{-1} wet weight in crabs) than the prescribed limit of FAO/WHO (0.3 mg kg^{-1} wet weight) from the studied area. The results of the present findings could be useful to develop effective management strategies for policy-makers and stakeholders.

Keywords*: Heavy metal assessment, fish, crab, Gulf of Khambhat, bio-concentration factor*

Introduction

The brunt of rapid growth, industrialization, and urbanization are faced by different ecosystems in the form of pollution and degradation. With the advancement of technologies, the standard of living has enhanced over the years. This has resulted in the release of unwanted substances into the ecosystems due to the ineffective regulation of pollution and emission control (Anyanwu *et al.,* 2018) particularly in sub-Saharan Africa (SSA). Excessive anthropogenic activities lead to heavy metal toxicity, micro-environment changes and ecosystem collapsing (Kawser *et al.,* 2011; Sharifuzzaman *et al.,* 2016). The ease of release of effluents in aquatic ecosystems has made them more vulnerable compared to other ecosystems.

Heavy metals are persistent environmental pollutants and human beings are exposed to them through water, air, food or industrial settings (Jan *et al*., 2015) which have widespread environmental distribution and originate from natural and anthropogenic sources, are common environmental pollutants. In recent decades, their contamination has increased dramatically because of continuous discharge in sewage and untreated industrial effluents. Because they are non-degradable, they persist in the environment; accordingly, they have received a great deal of attention owing to their potential health and environmental risks. Although the toxic effects of metals depend on the forms and routes of exposure, interruptions of intracellular homeostasis include damage to lipids, proteins, enzymes and DNA via the production of free radicals. Following exposure to heavy metals, their metabolism and subsequent excretion from the body depends on the presence of antioxidants (glutathione, α-tocopherol, ascorbate, etc). The biological buildup in the food chain allows multi-heavy metal pollutants to increase, with maximum effects on top predators (Afshan *et al.,* 2014). The ubiquity of heavy metals not only present great threats to benthic dwellers but also pose a high risk to fish, fish consumers and other wildlife, whose severity varies with age, susceptibility, nature of metal, method of exposure and duration of exposure. Owing to the various alterations stimulated by these heavy metals, in the physical, chemical and biological characteristics of aquatic ecosystems, there has been a continuous need to study them to get a clear picture of their pathways along with detrimental effects, keeping public safety in mind.

Keeping this in view, the present study was planned to evaluate the concentration of heavy metals in one of the most industrialized and urbanized states of India, *i.e.* Gujarat. Gujarat, with its longest coastline of 1600 km, not only ranks first in marine fish production but also lines high in chemical, petrochemical and oil-based industries. Gujarat's position as a leading industrial state in India could be established by the fact that it contributed 18.4% of India's total industrial output in 2017, the largest share among all states in India. Most of the industrialization in Gujarat has centered over South Gujarat due to its endowment with perennial rivers such as Narmada, Tapti, Sabarmati, Kolak, Par, Auranga, Purna, and Ambica. The ease of transportation, continuous water supply, lenient monitoring and surveillances measures have resulted in the dumping of toxicants in these aquatic habitats. Dudani *et al.* (2017) also highlighted similar scenarios where heavy metal contamination in mangroves along Gulf of Khambhat has been reported. Though a plethora of studies has been carried out along the Gulf of Khambhat and nearby estuaries, studies pertaining to heavy metal toxicity in benthic feeders are still lacking. Therefore, the present study was envisioned for 1) assessment of heavy metal in sediment 2) spatial variability of heavy metal along the coast of Kolak, Par, Auranga, Purna, and Ambica estuary 3) assessment of bio-accumulation in three bottom-feeder species namely *Mugil curema* (mullet), *Boleopthalmus dussumieri* (mudskipper), and *Scylla serrata* (mud crab). All three selected species form an important livelihood source for rural fishermen and contribute significantly to the South Gujarat fishery (Bhakta *et al*., 2018; Acharya *et al*., 2019).

Material and methods

Study area description

As mentioned above, the present study was carried out in the estuarine region of Kolak, Par, Auranga, Purna, and Ambica along South Gujarat, India (Fig. 1). All these rivers originate from eastern hilly highlands, namely Satpuda and Vindhyachal (Western Ghats) of Gujarat and meet the Arabian Sea on the South Gujarat coast. The estuaries' in the region are bi-diurnal, *i.e.* experience two low tides and two high tides in 24 hours and are surrounded by several small and medium towns as well as industrial clusters. The diurnal nature of these estuaries facilitate intermixing of nutrients, heavy metals, toxicants and other suspended solid matters. Gujarat Pollution Control Board (GPCB) has already listed highly polluting units and moderately polluting units along the region, thus generating the need for in-depth analysis of this ecosystem.

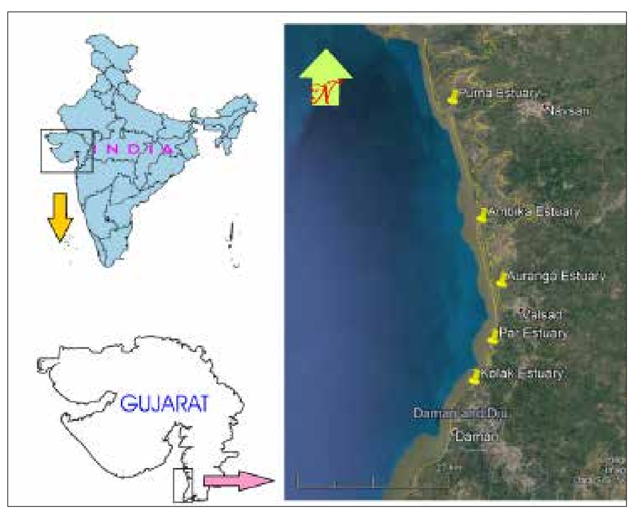


Fig. 1. Showing study area and sampling locations

Sampling strategy and heavy metal assessment in the estuarine region

The present study was carried out during 2015-2016 in pre monsoon and post monsoon season. The sediment samples were collected using a Grab sampler from each study site to estimate the heavy metal concentration in sediment. The samples were collected in triplicates from each sampling point then stored at 4ºC and transferred to the laboratory. In the laboratory, samples were stored -20ºC until further analysis. Then the samples were air-dried, and further, they were oven-dried at 48°C for 2 days to ensure all remaining moisture was evaporated by following the methodology of Defew *et al.* (2005), 10 g of sediment sample from each site was homogenized and stored in airtight labeled plastic bags.

Along with the sediment, three benthic species were selected to evaluate the concentration of heavy metal and bioaccumulation along the selected estuaries *i.e M. curema* (Mullet), *B. dussumieri* (mudskipper) and *S. serrata* (mud crab). The species selection was based on their economic importance, as all of them form lucrative fishery along the Indian coast. A minimum of 5-20 individuals of each species was collected from all the sampling sites depending on the fish catch. Each specimen was wrapped in extra heavy-duty aluminum foil, before sealing, labeling and final transfer into waterproof bags. The samples were stored in a dry ice-packed insulated box until the final transfer to the laboratory. In the laboratory, samples were thoroughly washed with distilled water and stored at −20°C. Total length and weight were recorded from thawed samples before muscle tissue collection. All the specimens were de-scaled and dried in an electric oven at 80°C for 3 h. These oven-dried samples were homogenously powdered and further packed in labeled airtight plastic bags. Both the dried powdered samples of fish tissues and sediments were thoroughly packed and sent to the Centre for Coastal and Marine Research in Tuticorin for the analysis of the heavy metal using Inductively Coupled Plasma–Mass Spectrometer (ICP-MS), following (AOAC, 1997) protocol.

The mean values with standard deviation for resultant data were calculated and Hierarchical Cluster Analysis (HCA) was used to quantitatively identify specific areas of heavy metal contamination. HCA was performed using the mean concentration of individual heavy metals to determine their similarity along the various sampling stations. HCA was carried out using squared Euclidean distance method (Lattin *et al*., 2003; Singh *et al*., 2005; Panseriya *et al*., 2020). All the analysis was executed using IBM SPSS statistics version 20.

Bio-concentration factor (BCF) in muscle tissue of different species

Additionally, the bio-concentration factor (BCF) which evaluates the total metal concentration in biota was also calculated. BCF was calculated to know whether or not the metals are bio-accumulated in the tissues of the fishes, to protect the consumers from exposure to the heavy metal toxicity. BCF was evaluated by following the methodology of Mountouris *et al.* (2002). BCF was defined as BCF=C_{biota} / C_{soil}, where C_{biota} and C_{soil} are the total metal concentration in biota and soil, respectively. BCF was calculated for selected metals (Zn, Pb, Cd, Hg, Cu) as follows

$$BCF = \frac{Cbiota}{Csoil/ambientmedium}$$

Where C_{biota} is the heavy metals concentration in the biota for fish and *C soil/ambient medium* the heavy metals concentration in sediment. If the values of BCF ranged above 1000 for the metal, it indicated high bio-accumulation and bio-magnification property by the metal, whereas if the values ranged below 30, the accumulation level by the metals were categories as low as per the BCF index (Potipat *et al.,* 2015)

Results

Spatial variability of heavy metals in estuarine sediments

The assessment of heavy metals revealed the presence of Pb, Cu, Cd, Hg, and Zn in sediment samples from all the selected estuaries. Lead was found to be the most abundant metal in sediment with the highest concentration from Par (42.01 ppm) Estuary followed by Kolak and Auranga, where the Pb concentration of 25.41 ppm and 24.74 ppm were recorded respectively. Purna Estuary showed the least concentration of Pb with 19.62 ppm. Copper was found to be the second most abundant heavy metal along the studied region. The maximum concentration of Cu was recorded from Kolak (17.02 ppm), followed by Ambica (15.26 ppm), Auranga (14.53 ppm), Par (13.83 ppm), and Purna (11.93 ppm). Moreover, maximum concentration of zinc and cadmium was recorded along Auranga Estuary (0.63 ppm and 7.14 ppm), while the least concentration of both the metals was observed in Kolak (0.38 ppm) and Par (4.34 ppm) respectively. The concentration of mercury was found to be highest at Par (0.90 ppm), while the least (0.09 ppm) from Auranga Estuary. Results of HCA analysis corroborated the above findings and revealed the presence of two clusters significantly different from each other based on the heavy metal concentration. Cluster one consisted of Kolak, Auranga, Ambica, and Purna where sediment quality was more or less similar, and the second cluster consisted of Par. Moreover, the results revealed that the concentration of Pb and Hg were higher at Par compared to the rest of the studied stations thereby forming major drivers for the difference in sediment quality. The findings could be attributed to various anthropogenic and industrial factors existing at Par (Fig. 2 & 3).

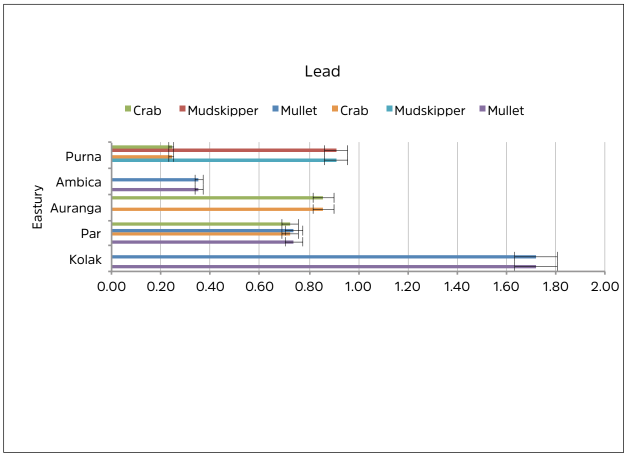


Fig. 2. Spatial distribution of heavy metals in estuarine sediments

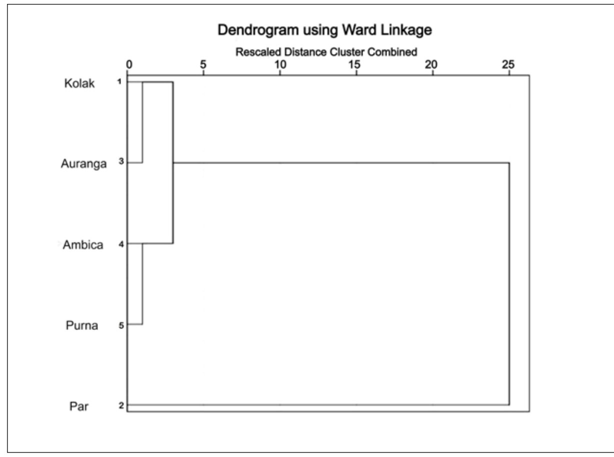


Fig. 3. Dendogram showing the cluster relationship among the four stocks

Assessment of heavy metal variability and bioaccumulation in tissue samples

Analysis of heavy metals at tissue level revealed species-specific preference. The results revealed that both the mullet and crab species had maximum concentration of zinc followed by copper whereas the mudskipper recorded a maximum concentration of copper followed by zinc. The average concentration of heavy metals in the muscle tissue of fishes and crab are presented in Fig. 3, Table 1, 2, and 3. The average concentration of metals in fish tissue varied in descending order of Cu 6.77 >Zn 5.60>Pb 0.37>Hg 0.19 >Cd 0.01 mg kg^{-1} ww (wet weight). Similarly, the heavy metal concentrations in crab

Table 1. Heavy metal concentration in *M. curema* along the study region

Heavy metal concentration (mg kg-1 ww) in Mullet (*Mugil curema)*					
Name of estury	Lead (Pb)	Copper (Cu)	Mercury (Hg)	Zinc (Zn)	Cadmium (Cd)
Kolak	1.72 ± 0.01	6.06 ± 0.01	0 ± 0.00	9.4 ±0.02	0.01± 0.00
Par	0.73 ± 0.01	3.18 ± 0.01	0 ± 0.00	4.67±0.01	0.02 ± 0.00
Auranga	0 ± 0.00	3.02 ± 0.01	0.35± 0.01	3.14±0.01	0.01 ± 0.00
Ambica	0.35 ± 0.01	4.60 ± 0.01	0 ± 0.00	4.55 ±0.01	0.03 ± 0.00
Purna	0 ± 0.00	7.07± 0.01	0.27 ± 0.01	6.45 ± 0.01	0 ± 0.00

Table 2. Heavy metal concentration in *B. dussumieri* along study region

Heavy metal concentration (mg kg-1 ww) in Mudskipper (*B. dussumieri*)					
Name of estury	Lead (Pb)	Copper (Cu)	Mercury (Hg)	Zinc (Zn)	Cadmium (Cd)
Kolak	0 ± 0.00	12.34 ± 0.03	0 ± 0.00	9.92 ± 0.01	0 ± 0.00
Par	0 ± 0.00	13.41 ± 0.01	0.31 ± 0.00	4.38 ± 0.01	0 ± 0.00
Auranga	0 ± 0.00	5.21± 0.01	0 ± 0.00	4.75 ± 0.01	0 ± 0.00
Ambica	0 ± 0.00	3.58 ± 0.01	01 ± .00	3.39 ± 0.01	0 ± 0.00
Purna	0.91 ± 0.00	9.13 ± 0.01	0 ± 0.00	5.26 ± 0.01	0.05 ± 0.00

Table 3. Heavy metal concentration in *S. serrata* along study region

Heavy metal concentration (mg kg-1 ww) in crabs (*S. serrata*)					
Name of estury	Lead (Pb)	Copper (Cu)	Mercury (Hg)	Zinc (Zn)	Cadmium (Cd)
Kolak	0 ± 0.00	3.76 ± 0.06	0.68 ± 0.06	8.32 ± 0.01	0 ± 0.00
Par	0.72 ± 0.01	8.87 ± 0.01	0.01 ± 0.00	17.07 ± 0.01	0.01 ± 0.00
Auranga	0.85 ± 0.01	6.03 ± 0.01	0 ± 0.00	5.01 ± 0.01	0 ± 0.00
Ambica	0 ± 0.00	3.32 ± 0.01	0 ± 0.00	3.71 ± 0.01	0.01 ± 0.00
Purna	0.24 ± 0.01	1.34 ± 0.01	0 ± 0.00	0 ± 0.00	0 ± 0.00

varied in the range of Zn 6.82 > Cu 4.67 > Pb 0.36 > Hg 0.14 >Cd 0.00 mg kg^{-1} ww.

Copper was found to be the most abundant heavy metal in tissue samples from the studied area. The maximum concentration of Cu was recorded in mudskipper, followed by mullet and crab. Mudskipper recorded the highest Cu concentration (13.4±0.01 mg kg^{-1} ww) from Par Estuary with an average of 8.7 mg kg^{-1} ww, while the minimum value of Cu was reported from Ambica Estuary (3.6±0.01 mg kg^{-1} ww) (Table 3). In the case of mullet maximum concentration of Cu, 7.08±0.01 mg kg^{-1} ww was recorded from Purna Estuary, with an average concentration of 4.79 mg kg^{-1} ww whereas least concentration 3.03±0.01 mg kg-[1] ww from Auranga Estuary (Table 2). Moreover, crabs recorded an average concentration of 4.67 mg kg^{-1} ww for Cu, with maximum concentration from Par Estuary (8.88±0.02 mg kg^{-1} ww) and lowest concentration from Purna Estuary (1.34±0.01 mg kg^{-1} ww) (Table 1).

Zinc was found to be the second most abundant metal in the study area. The average concentrations of Zn in mullet and mudskipper were recorded as 5.65±0.01 and 5.5 ±0.2 mg kg^{-1} ww respectively. Mudskipper recorded, the highest concentration of Zn (9.9±0.01 mg kg^{-1} ww) from Kolak whereas the lowest (3.4±0.01 mg kg^{-1} ww) from Ambica Estuary (Table 2). Similarly, mullet also revealed highest concentration (9.40±0.01 mg kg^{-1} ww) from Kolak, while the minimum concentration (3.15±0.01 mg kg^{-1} ww) was found along Auranga Estuary (Table 1). On the other hand, heavy metals in crabs revealed highest concentration of Zn (17.1±0.01 mg kg^{-1} ww) from Par and the least (0.0 mg kg^{-1} ww) along Purna Estuary (Table 3). The average concentration of Zn for crab samples ranged between nil to 17.1±0.01 (Par) with an average of 6.8 mg kg^{-1} ww (Table 3).

Lead which is seldom reported and forms one of the most toxic heavy metals was recorded from all the studied estuaries. Mullet samples recorded the highest concentration of Pb (1.72 mg kg^{-1} ww) from Kolak Estuary with an average concentration of 0.56 mg kg^{-1} ww (Table 1). The least concentration of 0.00 mg kg^{-1} ww was recorded from Purna and Ambica estuaries. Mudskipper recorded Pb concentration of 0.91±0.01 mg kg^{-1} ww only from Purna Estuary (Table 2). Similarly crab tissues showed an average concentration of 0.36 mg kg^{-1} ww with the highest concentration (0.86±0.01mg kg^{-1} ww) from Auranga Estuary whereas the least concentration 0.00 mg kg^{-1} ww from Kolak and Ambica estuaries (Table 3).

Cadmium in the sample tissues was in the order of mullet > mudskipper > crab. Cd in the mudskipper was reported only from Purna Estuary (0.05±0.01 mg kg^{-1} ww) (Table 2). In the case of mullet average concentration of Cd was 0.01 mg kg^{-1} ww,

Table 4. Bio-concentration factor along the study area in the selected species

BCF in Mullet							
Name of estuary	Lead (Pb)	Copper (Cu)	Mercury (Hg)	Zinc (Zn)	Cadmium (Cd)	BCF Range	Category BCF[a]
Kolak	0.52	1.82	0.00	2.82	0.00	>1000	Very high
Par	0.22	0.96	0.00	1.40	0.01	100-1000	High
Auranga	0.00	0.91	0.11	0.94	0.00	30-100	Moderate
Ambica	0.11	1.38	0.00	1.37	0.01	<30	Low
Purna	0.00	2.12	0.08	1.94	0.00		
BCF in Mudskipper							
Name of estuary	Lead (Pb)	Copper (Cu)	Mercury (Hg)	Zinc (Zn)	Cadmium (Cd)	BCF Range	Category BCF[a]
Kolak	0.0	2.47	0.00	1.98	0.00	>1000	Very high
Par	0.0	2.68	0.06	0.88	0.00	100-1000	High
Auranga	0.0	1.04	0.00	0.95	0.00	30-100	Moderate
Ambica	0.0	0.72	0.19	0.68	0.00	<30	Low
Purna	0.2	1.83	0.00	1.05	0.01		
BCF in crabs							
Name of estuary	Lead (Pb)	Copper (Cu)	Mercury (Hg)	Zinc (Zn)	Cadmium (Cd)	BCF Range	Category BCF[a]
Kolak	0.00	0.94	0.17	2.08	0.00	>1000	Very high
Par	0.18	2.22	0.00	4.27	0.00	100-1000	High
Auranga	0.21	1.51	0.00	1.25	0.00	30-100	Moderate
Ambica	0.00	0.83	0.00	0.93	0.00	<30	Low
Purna	0.06	0.33	0.00	0.00	0.00		

BCF[a] Potipat *et al.*, 2015

with the highest concentration of 0.03±0.01 mg kg^{-1} ww. Moreover the lowest concentration of Cd (0.0 mg kg^{-1} ww) was recorded from Ambica and Purna estuaries respectively (Table 1). Crab samples recorded a maximum concentration of 0.01±0.00 mg kg^{-1} ww from Par and Ambica and with no records from the rest of the estuaries (Table 3).

Mercury levels in the studied species were in the order of mudskipper > crab > mullet. The highest concentration of mercury was recorded from mudskipper samples (1.0 ±0.01 mg kg^{-1} ww) along Ambica Estuary followed by crab (0.68 ±0.00 mg kg^{-1} ww) along Kolak Estuary. Traces of mercury were also recorded from Auranga, Purna, and Par estuaries (Tables 1, 2, and 3).

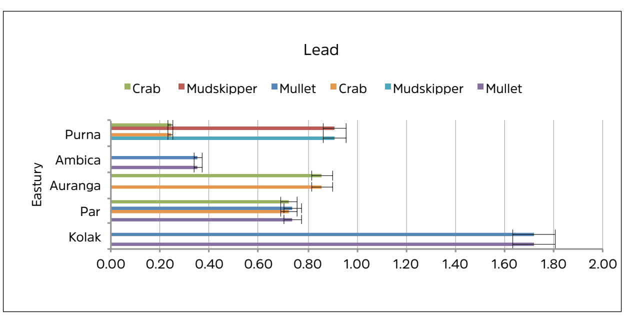
Bio Concentration Factor (BCF) index

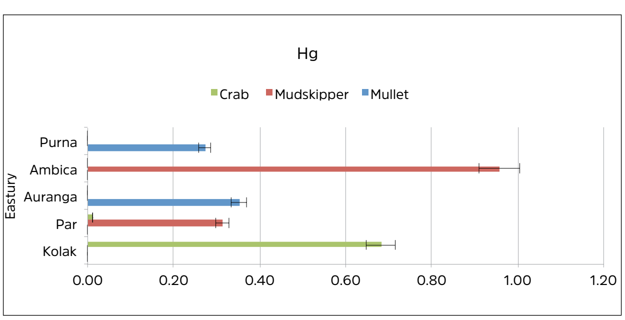
The results of the BCF are depicted in Table 4. Based on the BCF index and as evident from Table 4, all the species in the present study were categorized as "low" as per the BCF index. The bio-accumulation of heavy metals ranged between 0.00 – 4.27 for Zn, while 0.33 – 2.68 for Cu. The BCF for the remaining four heavy metals was very low and ranged from 0.00 –0.52 for Pb, 0.00 – 0.19 for Hg, 0.00 – 0.01 mg kg^{-1} ww for Cd.

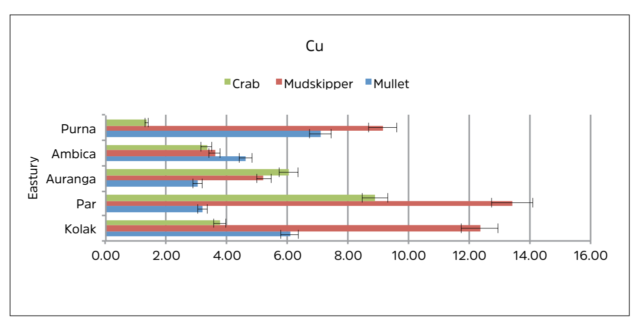
None of the species showed significant bioaccumulation of the concerning metal. Although recorded in low concentration, the presence of these heavy metals could not be ignored. The bioaccumulation factor calculated suggested that average bioaccumulation was highest in mullet (0.7) followed by crab (0.6) and mudskipper (0.6) *i.e.* mullet > crab> mudskipper. All three species showed a higher tendency of bioaccumulation for Zn and Cu (Fig. 5).

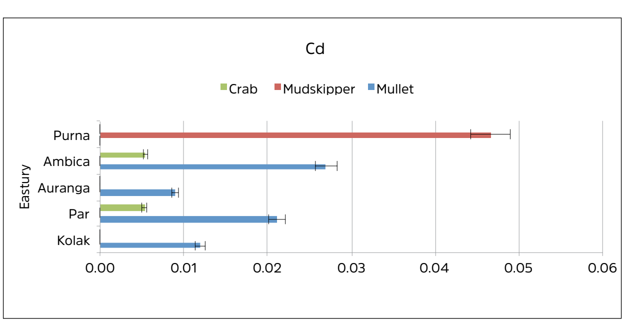
Discussion

The present study was undertaken to investigate accumulation of heavy metals in the muscle tissue of three commercially important fish species along the Gulf of Khambhat, as the concentration of heavy metals in commercially available fish was rarely investigated. The average metal concentrations from the aforementioned study were found to be, respectively for Cu, Zn, Pb, Hg and Cu as follows:, 4.79, 5.65, 0.56, 0.13 and 0.01 in mullet; 6.77, 5.60, 0.37, 0.19 and 0.01 in mudskipper and 4.67, 6.82, 0.36, 0.14 and 0.0 mg kg^{-1} ww in crab. Copper was found to be the most abundant heavy metal along the studied region with maximum mean concentration in mudskipper followed by mullet. Mudskipper displayed the highest mean concentration of Cu and Hg with the second-highest concentration of Pb and Cd. Copper a naturally occurring metal in the marine environment









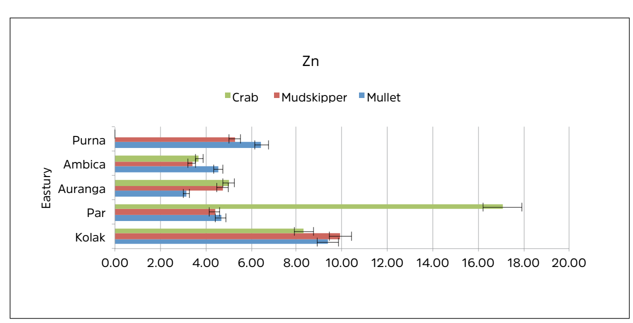


Fig. 4. Variability of heavy metal concentration in muscle tissue

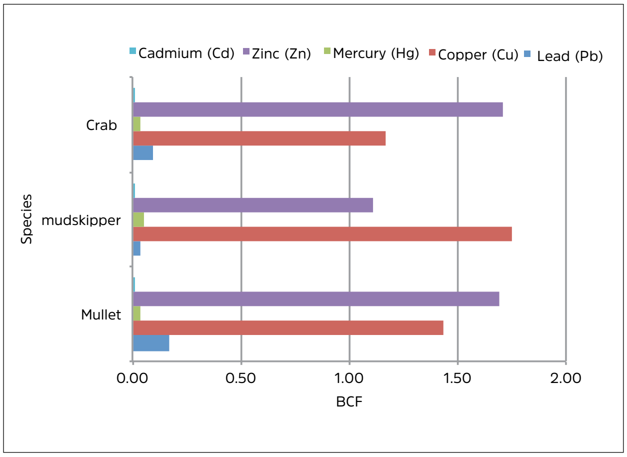


Fig. 5. Graph showing bio-concentration factor (BCF)

plays a significant role in the metabolism and physiological function of an organism. However, when present at elevated levels, Cu possess a great risk of acute and chronic toxicity. The results of the present study showed a mean concentration of 6.77 mg kg^{-1} ww in the case of fishes and 4.67mg kg^{-1} ww in the case of crab for Cu, findings which are five times higher than what has been documented by Jebakumar *et al.* (2015) and Patel *et al.* (2019) where the mean concentrations of 1.61 and 1.51 mg kg^{-1} ww have been reported. Although crabs have recorded an average copper concentration of 4.67 mg kg^{-1} ww from the studied region, a maximum concentration of 8.88 mg kg^{-1} ww was obtained from Par Estuary, similar to the findings of Jebakumar *et al.* (2015), where 8.86 mg kg^{-1} ww copper ion concentration has been reported. Cu concentration (341.04 μg/g), highest among Indian waters in mud crab has been reported from the Malanch region of Indian Sundarbans by Banerjee *et al.* (2006). Nevertheless, all the samples in the present study showed Cu below the prescribed limits of WHO standards which is 30 mg kg^{-1} ww (WHO/FAO 1984), hence nullifying the occurrence of copper toxicity from the studied area. Results of bio concentric factors revealed a mean concentration of 1.45 for Cu in all the species with maximum concentration from mudskipper (1.75). These findings were comparatively higher than Ahmed *et al.* (2011), where the authors reported BCF value of 0.05 and 0.06 in mud crab and mudskipper, respectively from Bangladesh. The authors have found maximum bio-concentration of copper in mudskipper, similar to the findings of the present paper.

Concentration for Zinc from other studied regions well agreed with our findings, where zinc was found to be one of the prominent heavy metal. Specifically, Jebakumar *et al.* (2015) found higher levels of Zn in crabs than fish species. The authors have reported an average concentration of 25.7 and 33.9 mg kg^{-1} ww for Zn in the case of fishes and crabs respectively along the Gulf of Khambhat. In the present study, fishes on an average recorded a concentration of 5.60 mg kg^{-1} ww, while crabs recorded an average concentration of 6.82 mg kg-1 ww, both of which are below the recommended levels of FAO/WHO (50 mg/kg). Studies by Banerjee *et al.* (2006) reported Zn concentration as high as 648.29 μg/g, in mud crab along Indian waters. Though zinc is considered nontoxic, the presence of Zn enhance the toxicity of cadmium to aquatic invertebrates (O' Neill, 1993).The high concentration of Zn along the studied region could be attributed to various anthropogenic activities. The vicinity of Par with Kolak rivers (Vapi), makes it recipient for the effluent discharge from the industrial hub. Vapi is the largest industrial area in Asia in terms of small-scale industries, dominated by chemical industries. Similar findings were obtained by Upadhyaya *et al.* (2014) where a high concentration of Zn was detected in groundwater. The authors attributed various anthropogenic activities as the prime cause of this augmentation. Zn showed the maximum BCF in crabs (1.71) followed by mullet (1.69) and mudskipper (1.10), findings that were deviating from the results of Ahmed *et al.* (2011), where maximum BCF for Zn has been reported in mudskipper than that of crab. The deviation in the results could be attributed to the difference in sediment quality, season, and availability of prey items for the studied species.

The present study investigated considerable levels of Pb toxicity, which were above the prescribed safety limits of FAO/WHO. All three studied species displayed a higher concentration of Pb than recommended by WHO standards (0.3 mg kg^{-1} ww). The maximum mean concentration was obtained in the case of mullet (0.56 mg kg^{-1} ww) followed by mudskipper (0.37 mg kg^{-1} ww) and crab (0.36 mg kg^{-1} ww). Mullet samples from Kolak (1.72 mg kg^{-1} ww) and Par (0.74 mg kg^{-1} ww) recorded the highest concentration of Pb. Samples of mudskipper from Purna Estuary also recorded a Pb concentration of 0.91 mg kg^{-1} ww. A maximum concentration of 0.72 mg kg^{-1} ww from Par and 0.86 mg kg^{-1} ww from Auranga has been obtained in the case of crabs. The present findings were five-time higher in the case of mullet and two times higher for mudskipper, while in the case of crabs the results were thrice the prescribed limit by FAO/WHO (2011), clearly indicating Pb toxicity along the studied region. The results were in accordance with the findings of Reddy *et al.* (2007) where Pb levels of 1.09 and 2.77 mg kg^{-1} ww has been reported from fishes and crabs. Pb bio-concentration of 0.09 and 0.04 has been reported for crab and mudskipper, findings which conform with the result of Ahmed *et al.* (2011), where Pb BCF of 0.02 for mud crab and mudskipper has been reported. The higher accumulation of Pb in the case of mullet could be attributed to its habitat and feeding behavior. Mullet tend to be near the sediment region (Bahnasawy *et al.*, 2009), feeding on detritus, diatoms algae, microscopic invertebrates, and fish parts (Olukolajo, 2008). Kilgour (1991) indicated that animals which have a close relationship with sediment, show relatively high body concentrations of metals. Similar to mullet, mudskipper also being a bottom feeder mainly feeds on diatoms, algal, plant material, nematode worms, harpacticoid copepod (Rathod and Patil, 2009) showed a considerable amount of Pb. As data on heavy metals in fish are related to the pollution status of the regions Hamza-Chaffai *et al.* (1996), the relatively high levels of metals in mullet and mudskipper caught from the Kolak, Par, Purna, and Auranga indicate potential pollution which could be because of the vicinity with Alang ship breaking yard. The results were corroborated by the findings of HCA analysis where Par formed one cluster segregated from other estuaries. The high Pb concentrations in the present investigation might be due to the discharge of various amounts of disposable solids, metal rust, and lubricants from the scrapping of ships and industrial activities in Alang shipyard.

Neither Cadmium nor Mercury was detected in alarming states from the studied region. Cd recorded a mean concentration of 0.01 mg kg^{-1} ww for fishes and 0.00 mg kg^{-1} ww for crabs. Mudskipper samples from Purna Estuary were found to be having a cadmium concentration of 0.05 mg kg^{-1} ww, which was less than the limits of FAO/WHO standards (0.5 mg kg^{-1} ww FAO/WHO, 2011) and indicate sparse Cd toxicity along the studied region. The present levels of Cd concentration in fishes were similar to those reported by Jebakumar *et al.* (2015) but lesser than reported by Reddy *et al.* (2007), where the authors reported a Cd concentration of 0.05 and 0.23 mg kg^{-1} ww respectively. Traces of mercury were also recorded from all the estuaries with maximum concentration along Ambica (1.0 mg kg^{-1} ww) from mudskipper, however, the concentration was in the limits of FAO/ WHO (0.5 mg/kg) nonetheless, their presence cannot be ignored.The sparse concentration of Cd and Hg in the present investigation might be due to the ship breaking operations and industrial activities and discharges of various amounts of enriched toxic substances to the studied area. Moreover, the unique tidal pattern on the Gulf of Khambhat, lead to the locking of various pollutants, heavy metals, and effluents from various source points, resulting in the present scenario. In terms of bio-concentration factors, none of the metals exceeded the limits, indicating that they are safe for human consumption.

Conclusion

The present study aimed to evaluate the heavy metal concentration and their accumulation in sediment and estuarine biota. Geochemical characterization of the present study indicated Pb, Cu, and Cd were high in the estuarine system. Moreover, sediment characterization from HCA analysis revealed that Par was statistically different from other estuaries, mainly due to the contamination of Pb and Hg. Additionally the results revealed that the studied species recorded highest concentrations for copper and the lowest concentration for cadmium. There was no single type of species that was consistently high for all metals. The results in the present study are attributed to various anthropogenic activities and heavy industrialization along the studied region, where the industrial waste finds an easy path to estuaries, pertaining to various small creeks, which enable the dumping to go unnoticed. All the studied species were in safe limits for human consumption, however, the results revealed critical accumulation of Pb along the south Gujarat estuaries. The detection of lead toxicity beyond the prescribed limits of FAO/WHO norms is of great concern with regard to the health of people, who are dependent on these species for their daily protein intake. Therefore results indicates that the accumulation of heavy metals in sediment and muscle tissue of benthic species was comparatively nonhazardous for human health except for Pb. Nevertheless, as the present study was conducted with limited sampling as well as sample size, further studies with increased number of samples and widespread sampling is required to strengthen the findings of the present study. It is anticipated that the results of the present study will be beneficial for all the stakeholders, industries, urban planners, and agencies that are responsible for taking necessary remedial measures for conservation of river water quality.

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References

Acharya, K. V., P. Dadhaniya, A. Shendage, A. Badne, and A. Chava. 2019. Estuarine Fisheries Resource of India. *Int. J. Sci. Appl. Res.*, 6(1): 1-12.

Afshan, S., S. Ali, U. S. Ameen, M. Farid, S. A. Bharwana, F. Hannan and R. Ahmad. 2014. Effect of different heavy metal pollution on fish. *Res. J. Chem. Environ. Sci.*, 2: 74–79.

Ahmed, K., Y. Mehedi, R. Haque and P. Mondol. 2011. Heavy metal concentrations in some macrobenthic fauna of the Sundarbans mangrove forest, southwest coast of Bangladesh. *Environ. Monit. Assess.*, 177(1-4): 505-514.

AOAC 1997. Association of Official Analytical Chemists Official Methods of Analysis (16th ed.), AOAC Intl., Gaithersburg, MD (1997)

Anyanwu, B. O., A. N. Ezejiofor, Z. N. Igweze and O. E. Orisakwe. 2018. Heavy Metal mixture exposure and effects in developing nations: An Update. *Toxics*, 6: 65.

Bahnasawy M., A. Khidr and N. Dheina, 2009. Seasonal variations of heavy metals concentrations in Mullet, *Mugil cephalus*, and *Liza ramada* (Mugilidae) from Lake Manzala, *Egypt. J. Appl. Sci. Res.*, 5: 845-852.

Banerjee, K., A. Mitra, R. Chakraborti, A. Das and D. Mukherjee. 2006. *Heavy metal concentrations in edible crab Scylla serrata in the Malancha region of India Sundarbans.* In A. Kumar (Ed.), Heavy metal pollution research. Delhi: Daya Publishing House, p. 210-218

Bhakta, D., W. Anand, G. Vaisakh, S. Kamble, T. Nirupada Chanu and S. Das. 2018. Mudskipper fishery and indigenous fishing devices in Narmada Estuary, Gujarat. *J. Indian Soc. Coastal Agric. Res.* 36(2): 74-78

Defew, L., J. Mair and H. Guzman. 2005. An Assessment of metal contamination in mangrove sediments and leaves from Punta Mala Bay, Pacific Panama. *Mar. Pollut. Bull.*, 50: 547–552.

Dudani, S., J. Lakhmapurkar, D. Gavali and T. Patel. 2017. Heavy metal accumulation in the mangrove ecosystem of south Gujarat Coast, India. *Turkish J. Fish. Aquatic Sci.*, 17: 755–766.

FAO/WHO, 2011. Joint FAO/WHO food standards program codex committee on contaminants in food.

Hamza-Chaffai A., M. Romeo and A. Abed. 1996. Heavy metal in different fish from the Middle Eastern coast of Tunisia. *Bull. Environ. Contam. Toxicol.*, 56: 766-773.

Jan, A. T., M. Azam, K. Siddiqui, A. Ali, I. Choi and Q. M. R. Haq. 2015. Heavy metals and human health: Mechanistic insight into toxicity and counter defense system of antioxidants. *Internat. J. Mol. Sci.*, 16: 29592–29630.

Jebakumar, J. P. P., G. Nandhagopal, S. Sundradarajan, M. Karuppasamy and S. Ragumaran. 2015. Eminence of heavy metal accumulation in fishes and crustaceans from the Gulf of Khambhat, India. *Curr. Sci.*, 109(3): 409–412.

Kawser, M. A., M. Das, M. Islam, M. Akter, S. Islam and M. Al-Mansur. 2011. Physico-chemical properties of tannery and textile effluents and surface water of river Buriganga and Karnatoli, Bangladesh. *World Appl. Sci. J.*, 12(2): 152-159.

Kilgour B. 1991. Cadmium uptake from cadmium–spiked sediments by four freshwater invertebrates. *Bull. Environ. Contam. Toxicol.,* 47: 70-75.

Lattin, J. M., J. D. Carroll and P. E. Green. 2003. Analyzing multivariate data. Pacific Grove, CA: Thomson Brooks/Cole. p. 351-352.

Mountouris, A., E. Voutsas and D. Tassios. 2002. Bioconcentration of heavy metals in aquatic environments: the importance of bioavailability. *Mar. Pollut. Bull.*, 44(10): 1136-1141.

O' Neill, P. 1993. Environmental chemistry. Chapan & Hall, Eds.. London. 268pp.

Olukolajo, S. 2008. The feeding ecology of *Mugil cephalus* (Linnaeus) from a high brackish tropical lagoon in south-west, Nigeria. *African J. Biotechnol.,* 7: 4192-4198.

Panseriya, H. Z., H. B. Gosai, A. O. Sankhwal, B. K. Sachaniya, D. J. Gavali and B. P. Dave. 2020. Distribution, speciation, and risk assessment of heavy metals: geochemical exploration of Gulf of Kachchh, Gujarat, India. *Environ. Earth Sci.*, 79: 1-10.

Patel, F. V., V. S. Makadia and A. D. Patel. 2019 Evaluation of heavy metal contamination in fish from the rivers of Gujarat and assessment of health risk associated with their consumption. *Curr. Top. Tox.,* 15:115-122.

Potipat, Jakkapan, Tangkrock-olan, Nongnud, Helander and Herbert. 2015. Bioconcentration Factor (BCF) and depuration of heavy metals of oysters (*Saccostrea cucullata*) and mussels (*Perna viridis*) in the river basins of coastal area of Chanthaburi Province, Gulf of Thailand. *Environment Asia*, 8: 118-128.

Rathod, S. and N. Patil. 2009. Feeding habits of *Bolephalmus bolephthalmus dussumieri* (cuv. and val.) from Ulhas river estuary near Thane city, Maharashtra State. *J. Aquat. Biol.*, 24: 153-159.

Reddy, M. S., B. Mehta, S. P. Dave, M. Joshi, L. Karthikeyan, V. S. Sarma, S. Basha, G. Ramachandraiah and P. Bhatt. 2007. Bioaccumulation of heavy metals in some commercial fishes and crabs of the Gulf of Cambay, India. *Curr. Sci.,* 92: 1489-1491.

Sharifuzzaman, S., D. M. H. Rahman, S. M. Ashekuzzaman, M. Islam, S. Chowdhury and M. S. Hossain. 2016. Heavy metals accumulation in coastal sediments. environmental remediation technologies for metal-contaminated soils: p.21-42.

Singh, C. K., A. Kumar, S. Shashtri, A .Kumar, P. Kumar and J. Mallick. 2017. Multivariate statistical analysis and geochemical modeling for geochemical assessment of groundwater of Delhi, India. *J. Geochem. Explor.*, 175:59-71.

Upadhyaya, D., M. D.Survaiya, S. Basha, S. K. Mandal, R. B. Thorat, S. Haldar, S. Goel, H. Dave, K. Baxi, R. H. Trivedi and K.H. Mody. 2014. Occurrence and distribution of selected heavy metals and boron in groundwater of the Gulf of Khambhat region, Gujarat, India. *Environ. Sci. Pollut. Res.,* 21(5): 3880-3890.